

## Chemical Variation as a Function of Lithotype and Depth in Victorian Brown Coal

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### Introduction

Victorian brown coal occurs in randomly sequenced stratified layers, known as lithotypes, which are distinguishable by their air-dried colour, maceral composition and many physical and chemical properties. The five major lithotypes can be related to generalized paleoenvironments of deposition and are known to influence many coal utilization parameters (1-3). Across the thick coal intervals which occur (up to 300 m) there is a small increase in coal rank observable via parameters such as % carbon and % volatiles (1). The purpose of this paper is to contrast the variation in the organic chemical nature of the coal occurring as a function of depth for a series of (nearly) identical lithotypes with that occurring as a function of lithotype. We have employed techniques giving both precise molecular level information (e.g., the distribution of extractable lipid classes) and average structural characterization of the whole coal (e.g., parameters derived from IR, solid state  $^{13}\text{C}$ -NMR, etc.). All of these techniques have been able to provide much deeper insights into the varying nature of the coal than the conventional elemental and functional group type analyses which have been carried out extensively in the past.

### Materials and Methods

Coal samples were taken from a single bore core (LY 1276) from the Flynn field in the Loy Yang region of the Latrobe Valley, Victoria, Australia. The core consists of > 100 m of continuous coal, but penetrates two coal seams, viz. Morwell 1A and Morwell 1B. These seams range from late Oligocene to Miocene in age. It is estimated that deposition of the 100 m of coal would have taken approximately 1 million years. Samples were chosen by visual examination of the air-dried colour of the coal. Lithotype classifications on this basis are usually, but not always correct; it was therefore found necessary to modify some of the initial classifications after a consideration of all the available petrographic and chemical data. This correction has not been incorporated in previous publications from our group (4). Further details relating to these samples, methods of fractionation and experimental techniques can be found elsewhere (5-6).

### Characterization of Whole Coals

Before considering the results of other more sophisticated analyses it is useful to demonstrate the divergent chemical nature of the coal lithotypes by a more classical approach. When elemental analytical data are expressed in bond equivalence form it can be seen (Figure 1) that there is some inherent spread in the plotted points for the suite of light lithotype samples. The different lithotypes are, however, readily distinguishable due to the much greater variance in their analytical figures. The distinguishing features are especially exhibited at the extremes of the lithotype classification as an increase in the number of bonds associated with carbon at the expense of hydrogen for the dark lithotype and visa versa for the pale lithotype. For the light samples the bond equivalent data are most consistent for carbon, with the mean values for hydrogen and oxygen exhibiting higher proportional standard deviations. The bond equivalence data implies that the difference between the lithotypes resides in the type of chemical structure(s) that the elements form.

There are only a few solid-state techniques capable of providing structural information on "whole" coals. The CP-MAS  $^{13}\text{C}$ -NMR spectra of Victorian brown coals exhibit significant fine structure including phenolic and carboxylic resonance envelopes which are consistent with their low aromaticity and rank. The proportion of aromatic carbon atoms,  $f(a)$ , in the coal can be determined from the spectra and the variation in this parameter across the sample suite is illustrated in Figure 2. While there is some spread in the  $f(a)$  values amongst the light samples ( $\bar{X} = 0.52$ ,  $\sigma = 0.03$ ) there is no obvious trend with depth. The variation as a function of lithotype transcends the inherent spread in the light samples and there is an obvious increase in aromaticity for the progression from paler to darker lithotypes. Only the medium-light sample cannot be adequately distinguished within the sample suite by this technique. In addition to their higher aromaticities the spectra of the medium-dark and dark lithotypes exhibit prominent phenolic and methoxyl carbon absorptions similar to the spectra of degraded lignins. Hence the variation in  $f(a)$  as a function of lithotype is considered to be predominantly the result of variation in the original organic input and in the relative preservation of various biopolymeric materials within the corresponding depositional paleoenvironments. Although aromaticity is known to correlate with coal rank over a wider regime, there is no suggestion of a regular increase in  $f(a)$  over the depth interval examined. The small variation in  $f(a)$  for the several light samples is probably a reflection of minor changes in the depositional paleoenvironments.

Absorption mode IR spectroscopy provides greater sensitivity for the observation of specific functional groups. The variation in the absorption coefficients  $K_{2920}$  (aliphatic C-H stretch) and  $K_{1710}$  (carbonyl, carboxyl stretch) across the suite of samples is illustrated in Figure 3. It is again obvious that the variation as a function of lithotype exceeds the spread inherent in the set of light samples. The proportional spread for the light samples is significantly more intense for  $K_{2920}$  ( $\bar{X} = 14.1 \text{ cm mg}^{-1}$ ,  $\sigma = 2.9$ ) than for  $K_{1710}$  ( $\bar{X} = 36.2$ ,  $\sigma = 2.2$ ), but in neither case is there any definitive trend with depth. A strong negative correlation ( $r = -0.95$ ) exists between  $K_{1710}$  and  $f(a)$  for all samples examined. The correlation between  $f(a)$  and  $K_{2920}$  is significantly lower ( $r = -0.84$ ) as would be expected from the higher proportional spread in the  $K_{2920}$  values. The structural implications of these relationships are not entirely clear, but the IR data provide a further clear indication of the effect of the depositional paleoenvironment upon the coal structure(s) which are ultimately preserved.

Rock-Eval analysis is a form of temperature programmed pyrolysis often applied to petroleum source rocks in which the level of evolved carbon dioxide and hydrocarbon-like material are quantitatively measured via oxygen (OI) and hydrogen (HI) indices. The temperature at which the maximum amount of volatile material is evolved ( $T_{\text{max}}$ ) is also recorded, and this can be related to the rank of the organic substrate. The average  $T_{\text{max}}$  values for the samples under consideration was observed to be  $397^\circ\text{C}$  ( $\sigma = 2.6$ ), a value which corresponds to a vitrinite reflectance of  $\sim 0.30$ . No significant regular variation in  $T_{\text{max}}$  was observed with either depth or lithotype and this method, also, does not provide any indication of the slight increase in rank over the 100 m coal interval. A plot of HI versus OI (Figure 4), however, provides a further method for distinguishing the lithotypes. Although there is a significant spread in the HI values for the light samples, the OI data enable better discrimination between the different lithotypes. This observation supports the NMR and IR data in suggesting that lithotype is a coal property especially influenced by the nature and concentration of oxygen containing species. HI is a measure of the hydrocarbon production potential and correlates strongly ( $r = +0.94$ ) with the percentage of extractable material (see later); it is a parameter which has substantial significance for coal-to-oil conversion. It can be seen that the lighter lithotypes and especially the pale sample provide greater potential in this respect.

## Characterization of Coal Fractions

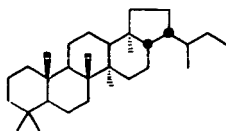
The variation in the weight percentage of total solvent extractable (TSE) material (extraction with chloroform/methanol/toluene) and solvent extractable humic acid (SEHA) for the coal samples is illustrated in Figure 5. There is a substantial reduction in the weight % of these fractions in the progression from paler to darker lithotypes. It can also be seen that the variation with lithotype is significantly more extreme than the variation within the suite of light lithotypes. Within the latter suite there is a notably large difference in the weight percentages between the two adjacent samples from 59 m and 78 m depth in the core. The jump across this interval can be related to the Morwell 1A/Morwell 1B seam boundary which occurs at the 73 m depth. Taking into account this aberration the data are consistent with an increase in extractable material as a function of depth (for samples within a particular lithotype classification and seam). The increase across the interval from 78 to 119 m depth is quite marked by comparison with the increase in extractable material which accompanies increasing rank within the subbituminous rank regime (7). There have been, however, no previous systematic studies giving any indication of what to expect within this lower rank interval. A more intense study of rank dependent phenomena within this interval could significantly enhance our understanding of coal forming processes.

The distributions of extractable n-alkanes from the different lithotypes are illustrated in Figure 6. All the distributions exhibit a marked predominance of odd carbon chain length homologues and in this respect all are similar to the distribution of n-alkanes which occur in living higher plant waxes. In other respects, however, the distributions differ markedly. For example, the dark lithotype exhibits a primary maximum at C<sub>29</sub> and a secondary one at C<sub>25</sub>. The medium dark and pale lithotypes exhibit only primary maxima at C<sub>31</sub> and C<sub>29</sub>, respectively. By contrast, all the light samples exhibit primary maxima at C<sub>29</sub> and secondary maxima at C<sub>37</sub>. These C<sub>37</sub> maxima appear to be a distinctive feature of the light samples and have almost certainly resulted from the input of some fairly specific taxon which was viable only in association with the paleoenvironment of deposition for this lithotype. The distribution can be further characterized by Carbon Preference Indices (CPIs), a parameter which is effectively the ratio of the abundance of odd relative to even carbon chain lengths. It can be seen (Figure 7) that there is considerable spread in the CPI values for the light samples and that only the CPI value for the dark lithotype lies significantly outside this margin. There is no apparent changes in the distribution of n-alkanes as a function of depth and it would appear that the distributions remain substantially representative of those contributed by the higher plant progenitors of the coal.

A consideration of the extractable n-fatty acid distributions gives a complementary characterization of the sample suite. The distributions are again a reflection of those observed in the higher plant precursors to the coal. The distributional differences between lithotypes and the similarities within a single lithotype classification are less obvious than in the case of the n-alkanes, but a statistical approach involving the determination of covariance between sample pairs was able to effectively differentiate the divergent nature of the distributional variations as a function of depth and lithotype (5). CPI values for the n-fatty acid distributions are plotted in Figure 8 (CPI, in this case, is effectively the ratio of even relative to odd chain lengths). Again there is a considerable difference in the values for the various lithotypes, but the spread of values within the light sample suite is relatively small. Within this spread, however, it is possible to discern a general reduction in the CPI values with depth. There is again a discontinuity across the seam boundary. There is a corresponding general reduction in the level of extractable n-fatty acids over this depth interval and the consistent variation in these two parameters is believed to indicate that progressive diagenetic removal and alteration of the fatty acids is occurring with depth within this coal sequence. The discontinuity across the seam

boundary is an indication of the complex combination of paleobotanical, geochemical and microbiological factors which control the diagenetic progression.

Many coals contain extended chain (> 31 carbon atoms) hopanes and related compounds which appear to be diagenetically derived from the lipids of certain procaryotic organisms. Biologically produced hopanoids exclusively possess 17 $\beta$ H,



17 $\beta$ H, 21 $\beta$ H-homohopane

21 $\beta$ H stereochemistry. The thermodynamically more stable 17 $\alpha$ H, 21 $\beta$ H stereochemistry has usually been explained to form in the geosphere via diagenetic acid catalyzed and temperature dependant isomerization from the biological diastereomers. Hence the diastereomeric ratio, 17 $\alpha$ H, 21 $\beta$ H/17 $\beta$ H, 21 $\beta$ H has been observed to rise in simulated maturation studies and with increasing depth of burial in sedimentary sequences. The present data exhibit a reversal of this trend; that is, there is a reduction in this ratio with depth for the series of light samples (Figure 9). Although there must be some mechanism to account for the formation of the abiological 17 $\alpha$ H, 21 $\beta$ H-diastereomers in the first place, the data suggest that 17 $\beta$ H, 21 $\beta$ H-diastereomers are being progressively produced with depth in the coal seam. On the basis of present understanding this could only occur by microbiologically mediated processes. The temperatures reached within the coal seam are obviously insufficient to force the isomerization towards its thermodynamic equilibrium. There is also a significant difference in the diastereomeric ratios determined by lithotype. This marked difference is probably substantially determined during the early stages of coal deposition where it may be significantly influenced by the pH of the surrounding swamp water or the coal surface acidity. The significant difference in the diastereomeric ratios (Figure 10) as a function of lithotype is consistent with the preceding explanation; that is, the dark lithotypes can be generally associated with higher acidities (and hence pH) which would favour the formation of the abiological isomer, as observed.

The polycyclic aromatic hydrocarbons (PAHs) in brown coal consist predominantly of pentacyclic angularly condensed hydroaromatic moieties. These compounds appear to be derived from C<sub>30</sub> triterpenoid precursors which occur as natural products in angiosperm waxes. It can be seen (Figure 10) that there is a marked variation in the concentration of PAHs as a function of both lithotype and depth. The variation as a function of lithotype is consistent with our views on the generalized paleo-environments of deposition, i.e., the lighter lithotypes are deposited in relatively anaerobic environments more conducive to the preservation of the originally deposited organic material, while the darker lithotypes are deposited in relatively aerobic environments in which much of the less resistant organic material is removed by oxidation or substantially altered microbiologically. The increasing concentration in PAH concentration with depth for the series of light samples suggests that the formation of PAHs is also occurring within the coal seam. It seems most likely that this transformation, too, is microbiologically mediated.

## Conclusions

The organic chemical nature of Victorian brown coal has been shown to vary as a function of both depth and lithotype. In the latter case the structural differences occur predominantly as a result of the differing nature of the depositional paleoenvironments and are readily distinguishable by both gross and molecular level parameters. The differences with depth are considerably more subtle and were observed only by specific molecular techniques; e.g., the level of PAHs, the diastereomeric ratio of hopanoids and the CPIs of the n-fatty acid distributions. Since the observed structural differences at the molecular level involve only a small proportion of the total coal substrate (parts per thousand level) it is hardly surprising that they are not manifested at the gross structural level. Although mild increases in temperature certainly occur across the sampled coal interval, the specific nature of the chemical changes observed with depth suggests that microbiological processes rather than geochemical (temperature dependent) processes are chiefly responsible. It may be that the warmer conditions deeper in the seam favour the viability of anaerobic microorganisms which can modify the coal substrate in the required manner, or more probably that the closer proximity of the deeper samples to underground aquifers (and potential sources of oxygen and inorganic nutrients) favour the viability of aerobic microorganisms.

## Acknowledgements

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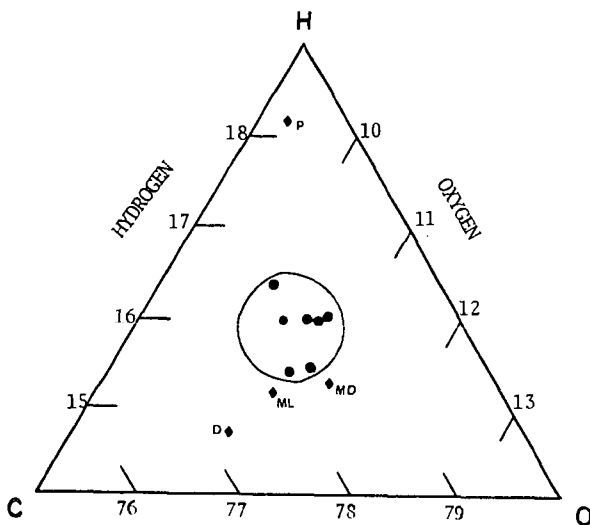


Figure 1 Ternary % bond equivalence diagram for whole coal samples.  
 • - Light lithotype samples; ♦ - other lithotypes as labelled:  
 P - pale, ML - medium light, MD - medium dark, D - dark.

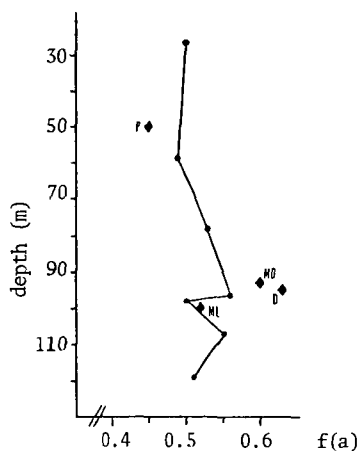


Figure 2 Aromaticity versus depth.  
 Data for the light lithotype samples  
 are joined to illustrate the spread  
 of values.

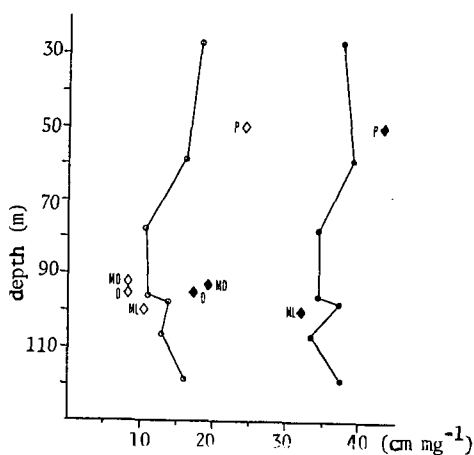


Figure 3 Infrared absorption  
 coefficients versus depth. Closed  
 symbols refer to  $K_{1710}$ ; open symbols  
 refer to  $K_{2920}$ .

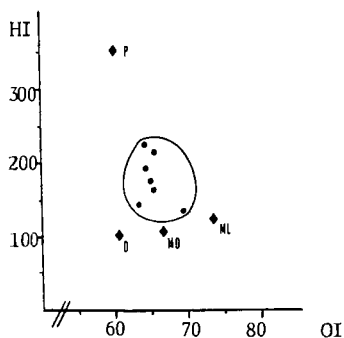


Figure 4 Hydrogen index (HI, mg HC/g TOC) versus oxygen index (OI, mg CO<sub>2</sub>/g TOC) from Rock-Eval analysis.

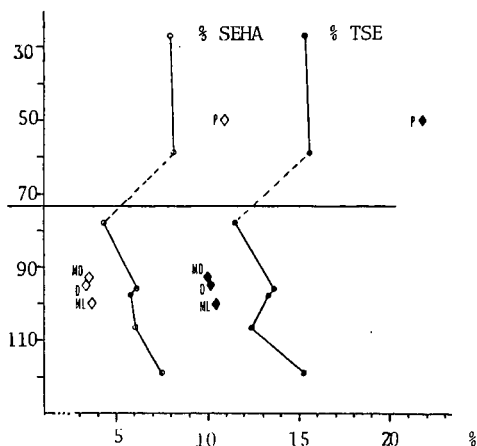


Figure 5 Weight % TSE (closed symbols) and SEHA (open symbols) versus depth. The horizontal line at 73 m represents the Morwell 1A/Morwell 1B seam boundary.

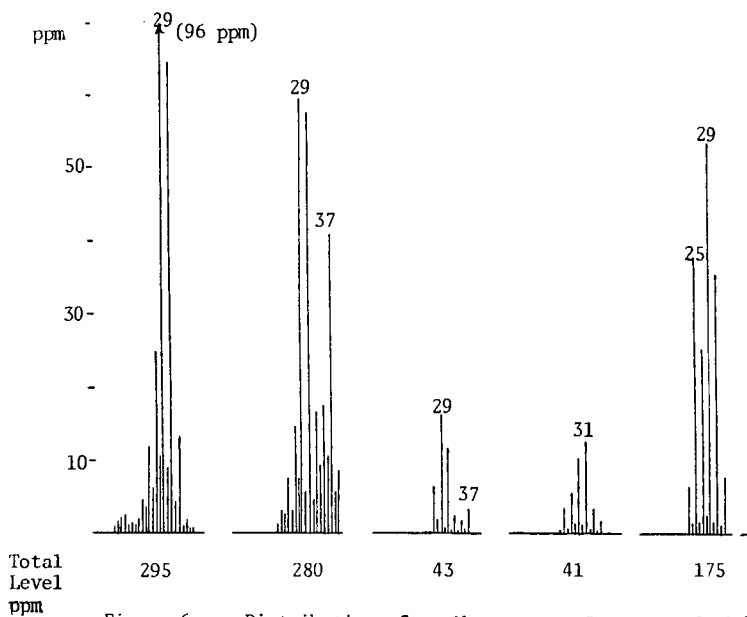


Figure 6 Distribution of n-alkanes as a function of lithotype.

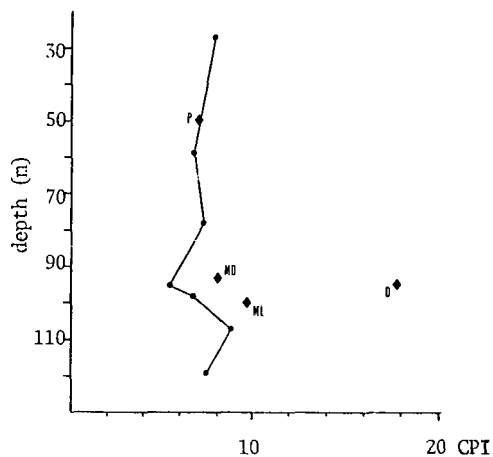


Figure 7 Carbon Preference Indices of n-alkanes versus depth.

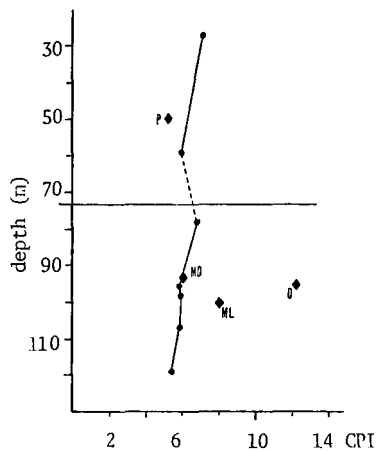


Figure 8 Carbon Preference Indices of n-fatty acids versus depth.

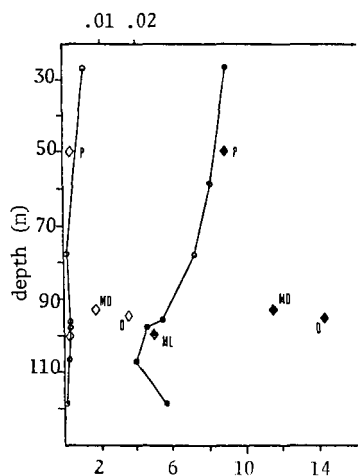


Figure 9 Ratio of diastereomers,  $17H,21H/17H,21H$ , for homohopane (closed symbols, bottom axis) and biohomohopanoic acid (open symbols, top axis).

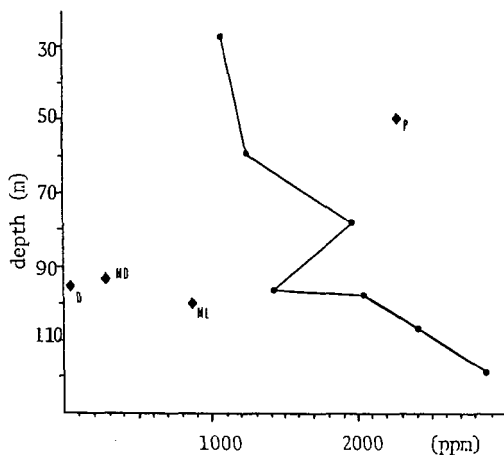


Figure 10 Level of extractable polycyclic aromatic hydrocarbons versus depth.